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STUDY OF POWDERED CARBONS FOR WASTE WATER TREATMENT & METHODS FOR THEIR APPLICATION

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STUDY OF POWDERED CARBONS FOR WASTE WATER TREATMENT AND METHODS FOR THEIR APPLICATION

~~by~~

West Virginia Pulp and Paper Company
Covington, West Virginia ~~24426~~

for the

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
DEPARTMENT OF THE INTERIOR

Contract ~~Number~~ 14-12-75

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ABSTRACT

Eleven commercial and experimental powdered activated carbons were subjected to an intensive laboratory evaluation of their physical and adsorptive properties to select those best suited to treating municipal waste water and to gain insight into properties important for this application. Measurements were made of TOC (Total Organic Carbon) adsorption isotherms from Roanoke, Virginia municipal secondary effluent, pore structure, BET surface area, molasses value, decolorizing index, iodine value, real density, suspendability, and apparent density. Correlations were made between capacities for adsorbing organic impurities from municipal secondary effluent, as measured by TOC adsorptive capacities, and carbon properties such as iodine value, molasses decolorizing index and pore structure.

Aqua Nuchar and Hydrodarco were clearly superior to other commercial grades tested in TOC adsorptive capacity per unit cost. The coal-base experimental carbons, pulverized Nuchar WV-L and Nuchar WV-W, were indicated by the suspendability test to be more easily removed than other carbons.

Among many pore structure parameters compared, surface area in pores greater than approximately 14 Angstroms in radius was found to give the best correlation with TOC capacity. However, the correlation was not perfect, the correlation coefficient being 0.91. TOC adsorptive capacity was indicated reasonably well by the decolorizing index test. Here, correlation coefficients in the 0.80's were obtained. It is suggested that the best carbon for adsorbing organics from municipal wastes have a broad spectrum of pore sizes. Particle size of the powdered carbons was found to strongly affect the rate of adsorption.

Aqua Nuchar, Hydrodarco, and pulverized Nuchar WV-L are recommended for further study.

INTRODUCTION

The studies presented in this report were sponsored by the Federal Water Pollution Control Administration, under Contract No. 14-12-75.

As commonly practiced, treatment of municipal waste is accomplished by a combination of settling and biological processes that remove some 85-90% of the organics present in the raw waste. These are so-called primary and secondary processes. In many highly populated and industrialized areas, primary and secondary treatment will not be capable of sufficiently reducing the organic pollution load to the receiving waters, and more complete treatment will be necessary. Furthermore, as demand for water for drinking and industry increases, increasing attention is being given to renovating waste water to remove essentially all impurities present following conventional treatment.

The only proven practical means for removing residual dissolved organic compounds is adsorption on activated carbon.

The ability of powdered activated carbon to remove organics from water is well recognized. Powdered carbon has been used for many years to remove the organic compounds which cause tastes and odors in drinking water (1). Only recently, however, have they been applied to treating waste water (2,3,4). Davies and Kaplan (2) have concluded that the optimum powdered carbon waste water process is one which uses flocculation-clarification in a two-stage countercurrent process.

Obviously, the properties of the carbon used are of primary importance. The carbon must have a high adsorptive capacity for the organic pollutants, attain a close approach to equilibrium in a reasonable period of time, and be readily removed by flocculation and clarification.

Some previous work has been performed to determine which basic carbon properties are important for superior performance in treating waste water. Studies by O'Conner, et al., (5) have shown no strong correlation between COD adsorption ability and BET surface area or ability to adsorb four specific model substances.

One of the critical steps in the powdered carbon process is the removal of the carbon from the water. Previous studies (2,3,4) indicated the need for flocculating aids to achieve carbon removal; however, development of a powdered carbon which settles without flocculating aids could substantially reduce costs.

The objective of the present study was the characterization of commercial and experimental carbons to select those best suited for municipal waste water treatment and to determine properties responsible for high adsorptive capacity for organic pollutants, high rate of adsorption, and ease of removal by settling.

Eleven commercial and experimental powdered activated carbons from a variety of sources were subjected to an intensive laboratory evaluation

to determine their physical and adsorptive properties. Emphasis was placed on the elucidation of the relationship between carbon adsorptive capacities for pollutants in municipal waste water and other properties of the carbon.

MATERIALS

The eleven carbons studied are described below:

1. Aqua Nuchar: A lignin-base commercial carbon produced by Westvaco and used for taste and odor control in municipal water treatment. 1967 cost for truckload or carload bag shipment was $150/ton, F.O.B. plant.

2. Nuchar C-115: A lignin-base commercial decolorizing carbon produced by Westvaco and used in sugar purification, chemical processing, and the manufacture of pharmaceuticals. 1967 cost for truckload or carload bag shipment was $239/ton, F.O.B. plant.

3. Nuchar C-115 Granular: The same carbon as C-115 except that it is of larger particle size. Cost is not available for this non-standard carbon.

4. Nuchar C-190: A lignin-base commercial decolorizing carbon produced by Westvaco and similar to C-115 except that it has higher adsorption capacity. It has similar uses to C-115. 1967 cost for truckload or carload bag shipment was $269/ton, F.O.B. plant.

5. Nuchar C-1000: A lignin-base commercial decolorizing carbon produced by Westvaco and similar to C-115 and C-190, but with exceptionally high adsorptive capacity. This carbon is used when a minimum carbon dosage is desirable to obtain maximum adsorption. 1967 cost for truckload or carload bag shipment was $1,470/ton, F.O.B. plant.

6. Pulverized Nuchar WV-W: This is a pulverized sample of Westvaco's Nuchar WV-W 8 x 30, a coal-base granular carbon for municipal and industrial water treatment. 1967 cost for carload or truckload bag shipment was $420/ton, F.O.B. plant.

7. Pulverized Nuchar WV-L: This is a pulverized sample of Nuchar WV-L 8 x 30, a coal-base carbon similar to WV-W except that it has a larger average pore size and a higher adsorption capacity. It is used for decolorizations, chemical processing, and waste water treatment. It is produced by Westvaco. 1967 cost for carload or truckload bag shipment was $520/ton, F.O.B. plant.

8. Pulverized Filtchar: A wood-derived carbon similar to Aqua Nuchar, but with a somewhat higher density. 1967 cost for truckload or carload bag shipment was $150/ton, F.O.B. plant.

9. Non-Pulverized Filtchar: The same as pulverized Filtchar except that it is of larger particle size. No costs are available for this non-commercial carbon.

10. Hydrodarco: A lignite-base commercial carbon for municipal and industrial water treatment, produced by Atlas Chemical Industries. 1967 cost for truckload or carload bag shipment was $150/ton, F.O.B. plant.

11. Darco G-60: A lignite-base commercial decolorizing type carbon produced by Atlas Chemical Industries and used in sugar refining and various chemical purifications. 1967 cost for truckload or carload bag shipment was $790/ton, F.O.B. plant.

The source of municipal waste water for this study was the Roanoke, Virginia Sewage Plant. The Roanoke sewage plant serves the entire Roanoke Valley and has a history of being a well-operated plant. Secondary treatment is provided by the activated sludge process. The Roanoke sewage plant is the closest source of domestic activated sludge effluent to Covington, Virginia, the location of Westvaco's Carbon Technical Center. A summary of the Roanoke sewage plant operations for 1967 is given below:

Flow, 18.6 MGD
Population Served, 149,000
Influent BOD, 240-270 mg/l (35% is of Industrial Origin)[a]
BOD Removal, 90%
Suspended Solids Removal, 90%

[a]The amount of industrial waste was estimated assuming a per capita loading of 0.17 lbs. BOD per day.

EXPERIMENTAL PROCEDURES

The experimental procedures to which the carbons were subjected are described below:

Molasses Value

In the Molasses Value (MV) procedure, the carbon sample is boiled with a standard molasses solution, filtered, and a (Klett-Summerson) colorimetric reading taken on the filtrate. From a calibration curve, the MV is read. In the preparation of the calibration curve, eight given weights of a standard 150 MV carbon are contacted with the standard molasses solution. The eight given weights of standard carbon are assigned a predetermined MV which does not change. The Klett readings obtained when contacting the eight standard carbon weights with the molasses solution are used for drawing an isotherm from which is determined the MV of the unknown sample. The molasses value is reported as being an approximate indication of pores greater than about 14 Angstroms in radius (6).

Decolorizing Index

In this test, the experimental procedure is the same as for the Molasses Value test, but the results are given in a fashion that is, in effect, a relative efficiency. Approximately, it is the ratio of molasses color capacity of a carbon to that of a standard carbon, times 10. The equation relating the Decolorizing Index (DI) to the Molasses Value is as follows:

$$DI = 19.956 \log MV - 29.912$$

Iodine Value

In the Iodine Value test, the weighed carbon sample is contacted with a standard 2.70 g/l iodine solution and filtered. The amount of iodine remaining in the filtrate is determined either colorimetrically or by titration. The iodine value is calculated as the percent of iodine adsorbed from solution. The iodine value is an indication of pores larger than about 5 Angstroms in radius (6) and is a rough measure of total surface area.

Suspendability

The suspendability is intended as a measure of ease of settling for powdered carbons and was first applied some years ago to carbons for municipal water treatment. For this test, a 200 mg/l concentration of carbon is mixed in distilled water and placed in a one-liter graduated cylinder. The carbon mixture is allowed to settle under quiescent conditions for a given time. The top 500 ml of liquid is siphoned off and the carbon remaining in this supernatant is measured. Suspendability is expressed as the percent of carbon in the supernatant liquid.

Apparent Density

In this test, 10 g of powdered carbon are placed in a 100-ml graduated cylinder and the sample tapped a given number of times on a Tap-Pak Volumeter. The packed volume is determined and the apparent density is calculated.

BET Surface Area and Pore Size Distribution by the Nitrogen Method (7)

These two properties were calculated from nitrogen adsorption isotherms ($78^{o}K$) and determined with a McBain-Bakr adsorption apparatus. Calculations were performed by Control Data Corporation on a CDC 3600 computer.

Basically, the calculation for surface area determines the quantity of gas necessary to form a mono-molecular layer on the carbon surface. By using known values for the area occupied by each molecule, the surface area of the carbon is computed. The method used was the BET (Brunauer-Emmett-Teller) method.

Pore size distributions were calculated using Roberts' (8) technique applied to the nitrogen isotherms. During adsorption, as the nitrogen pressure is increased, nitrogen gas condenses in ever larger capillaries, or pores, of the adsorbent. Measurements are made of the quantity of gas adsorbed for each increase in pressure. By use of the Roberts' procedure, which uses the correlation between relative pressure and size of pores in which capillary condensation is taking place (Kelvin equation), and makes correction for nitrogen adsorption on the surface of the pores, the pore volume in pores between various size intervals is calculated. By this method, pore radii from 10 to 1,000 Angstroms can be measured.

In the McBain adsorption apparatus, the carbons were first outgassed by simultaneously heating to $300^{o}C$ and evacuating down to 0.05 microns Hg pressure. Nitrogen isotherms were measured at liquid nitrogen temperatures ($78^{o}K$).

Pore Size Distribution by the Mercury Penetration Method

Pore size distributions by the mercury penetration method were determined with an Aminco-Winslow, 15,000 psi model porosimeter. For this test, the carbon is immersed in mercury and subjected to increasing pressures. Mercury, a non-wetting material, will enter smaller capillaries as pressure is increased. The amount of mercury forced into the pores of the carbon is measured at specified pressure intervals. Knowing the contact angle and surface tension of the mercury, pore sizes into which the mercury penetrates can be correlated with pressure. The mercury porosimeter measures pores from 75 to greater than 100,000 Angstroms in radius. In this study, it was used to measure pores from 1,000 to 100,000 Angstroms.

Real Density

Real density is the density of the carbonaceous "backbone" of the carbon after eliminating the effect of the pores. Real density is frequently

determined by helium displacement. In these studies, it was measured by a combination of nitrogen adsorption and mercury porosimeter data. Procedures for obtaining nitrogen adsorption and mercury porosimeter data were discussed above.

In the mercury porosimeter, at the highest pressures attained, pores down to 75 Angstroms in radius are filled. The volume of mercury used to fill the container and fill the pores is measured. The volume of the empty container minus the volume of mercury added gives the volume occupied by the solid carbon plus the volume in pores smaller than 75 Angstroms in radius. The McBain nitrogen adsorption data are used to determine the volume in pores smaller than 75 Angstroms. Knowing the weight of sample used and volume of solid carbon allows for determination of the real density.

TOC (Total Organic Carbon) Adsorption Isotherms

TOC (Total Organic Carbon) isotherms were determined by a batch contacting procedure. The procedure consisted of contacting 200 ml portions of the Roanoke municipal secondary effluent with known weights of powdered carbon followed by filtration and TOC analysis. The carbon and waste water were contacted for 90 minutes.

Loading on the carbon for each sample is calculated with the expression:

$$X/M = \frac{(C_o - C_f)\ V}{M}$$

where X/M is the TOC loading, C_o is original (filtered) TOC, C_f is the TOC after contacting and filtering, V is the volume of Solution (200 ml), and M is the weight of carbon.

Isotherms were plotted on log-log paper. A straight line on this plot indicates adherence to the Freundlich equation, as will be discussed below.

The isotherms were determined within 12 hours following collection of the waste water. These water samples were stabilized by the addition of ½ ml of saturated mercuric chloride solution per liter of water. A Beckman Laboratory Carbonaceous Analyzer was used for the TOC determinations. Duplicate TOC's were determined for all analyses.

Rate of Adsorption

For the rate of adsorption determination, a six (6.0) g sample of the carbon was added to a two (2.0) liter sample of Roanoke secondary effluent. Following this, the carbon-waste water mixture was stirred by a chain stirrer at 5,000 rpm, and at specified time intervals 25 ml samples were withdrawn, immediately filtered through fiberglass filter paper, and TOC's determined.

Particle Size Distribution

Particle size distributions were determined by use of an Alpine Jet Sieve. In this test, a given amount of material is placed on a sieve and a negative pressure (3.2 inches of water) produced by a vacuum cleaner. The suction is applied through a rotating slotted nozzle which sucks the fines-laden air downward through the sieve. The amount of material remaining on the sieve is determined and the percent passing calculated. The operating conditions for each sieve analysis are as follows:

Sieve Opening (Microns)	Initial Weight of Carbon (grams)	Sieving Time Minutes
149	10.0000	3/4
74	5.0000	2
44	5.0000	6
20[a]	0.1000	10
5[a]	0.1000	10

[a] The only way found to clean the 20-micron and 5-micron sieves was with a sonic bath.

RESULTS

Table 1 contains a summary of results for Molasses Value, Decolorizing Index, Iodine Value, Real Density, BET Surface Area, Suspendability for 10 and 30 minutes settling, and Apparent Density for each of the eleven carbons under study.

Figure 1 presents the TOC adsorption isotherms for Roanoke municipal secondary effluent determined on December 5, 1967. Figure 2 represents isotherm results obtained January 30, 1968. The initial filtered TOC's for the isotherms of December 5, 1967 and January 30, 1968 were 35.0 and 19.3 mg/l, respectively. An attempt was made to draw the best smooth curve between the points for each carbon.

Figures 3 and 4 present TOC adsorption rates for Aqua Nuchar, Hydrodarco, pulverized Nuchar WV-L and pulverized Filtchar, determined March 1968 on Roanoke municipal secondary effluent. These particular carbons were selected for rate studies since they represent four entirely different raw materials and are good candidates for study in later continuous adsorption studies.

Figure 5 presents particle size distributions of Aqua Nuchar, Hydrodarco, pulverized Nuchar WV-L and pulverized Filtchar. The Alpine Jet Sieve was used in these determinations.

Figures 6 and 7 show the pore size distributions in the range of 10 to 100,000 Angstroms radius for the eleven carbons. The pore-size distributions in the range of 10 to 1,000 were calculated from nitrogen isotherms, and pore size distributions from 1,000 to 100,000 were determined by the mercury penetration method. Distributions from these two sources were joined at 1,000 Angstroms radius.

Table 1
PROPERTIES OF POWDERED CARBONS

Property	Aqua Nuchar	Nuchar C-115	Nuchar C-115[1] Granular	Nuchar C-190	Nuchar C-1000	Pulv. Nuchar WV-W[2]	Pulv. Nuchar WV-L[2]	Pulv. Filt-char	Non Pulv. Filt.	Hydro-darco	Darco G-60
Molasses Value[3]	80	124	125	199	1,000	89	194	62	42	139	206
Decolorizing Index[3]	8.1	11.9	11.9	16.0	30.0	9.0	15.7	5.9	2.5	12.9	16.3
Iodine Value	93.3	95.6	95.4	94.6	95.3	94.2	96.7	81.4	79.9	78.0	70.0
Real Density - g/cc	1.86	1.72	1.80	1.88	1.86	2.54	2.49	1.98	2.18	1.85	1.95
Suspendability - %											
a. Ten (10) min.	81.9	80.3	53.6	76.5	78.1	33.1	28.6	73.1	22.9	66.1	41.4
b. Thirty (30) min.	60.0	81.2	43.1	65.2	63.7	23.2	22.2	48.0	18.8	41.9	29.3
Apparent Density - #/ft^3	15.2	14.0	9.6	12.7	9.8	43.8	32.4	21.5	21.2	30.8	23.5
BET Surface Area - m^2/g	754	811	804	841	998	905	1138	647	647	523	467

NOTES:

(1) Experimental carbon.
(2) Grades not now in production.
(3) Average of duplicate tests.

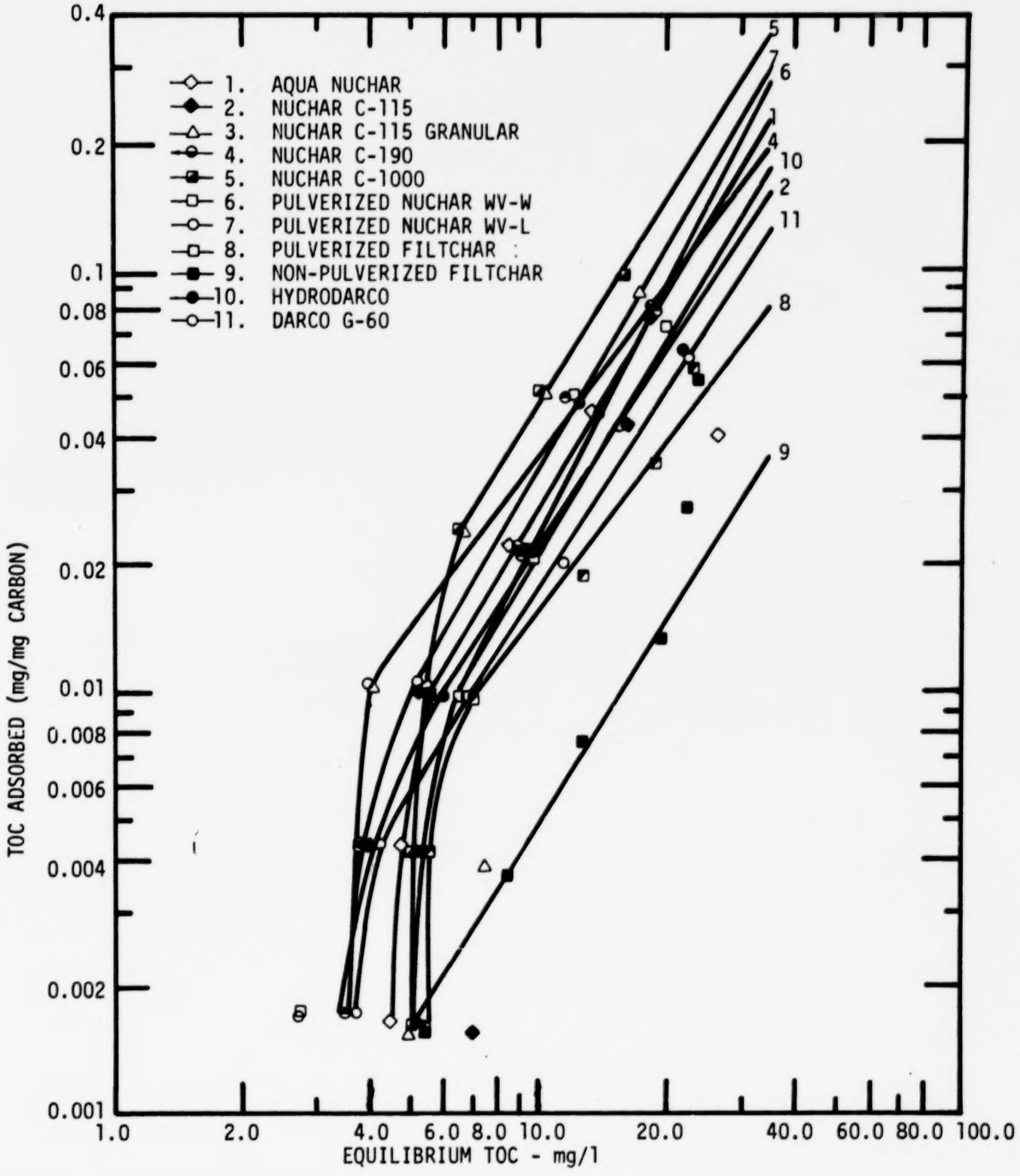

Figure 1. TOC adsorption isotherms
Roanoke, Virginia municipal secondary effluent, December 5, 1967

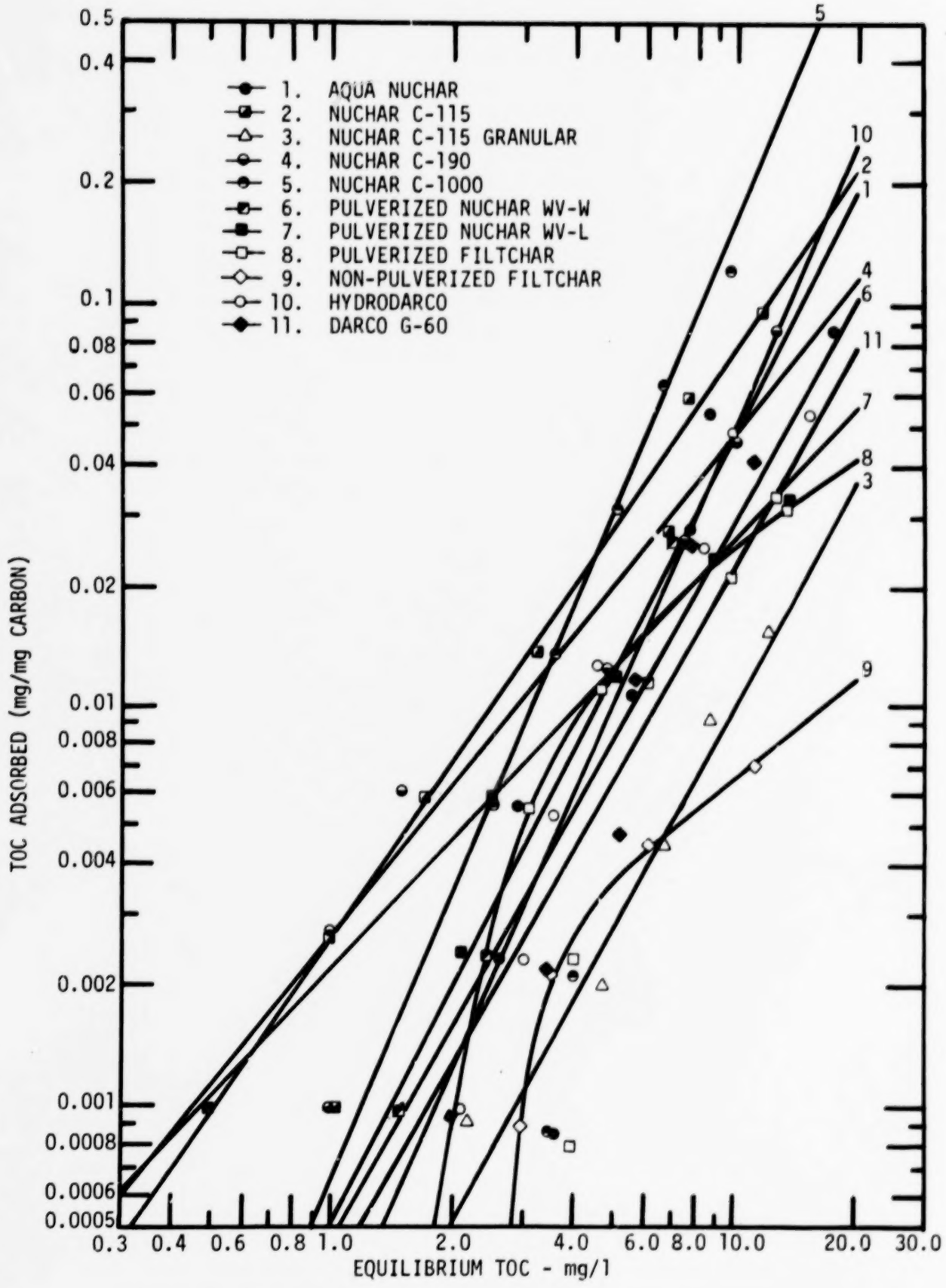

Figure 2. TOC adsorption isotherms
Roanoke, Virginia municipal secondary effluent, January 30, 1968

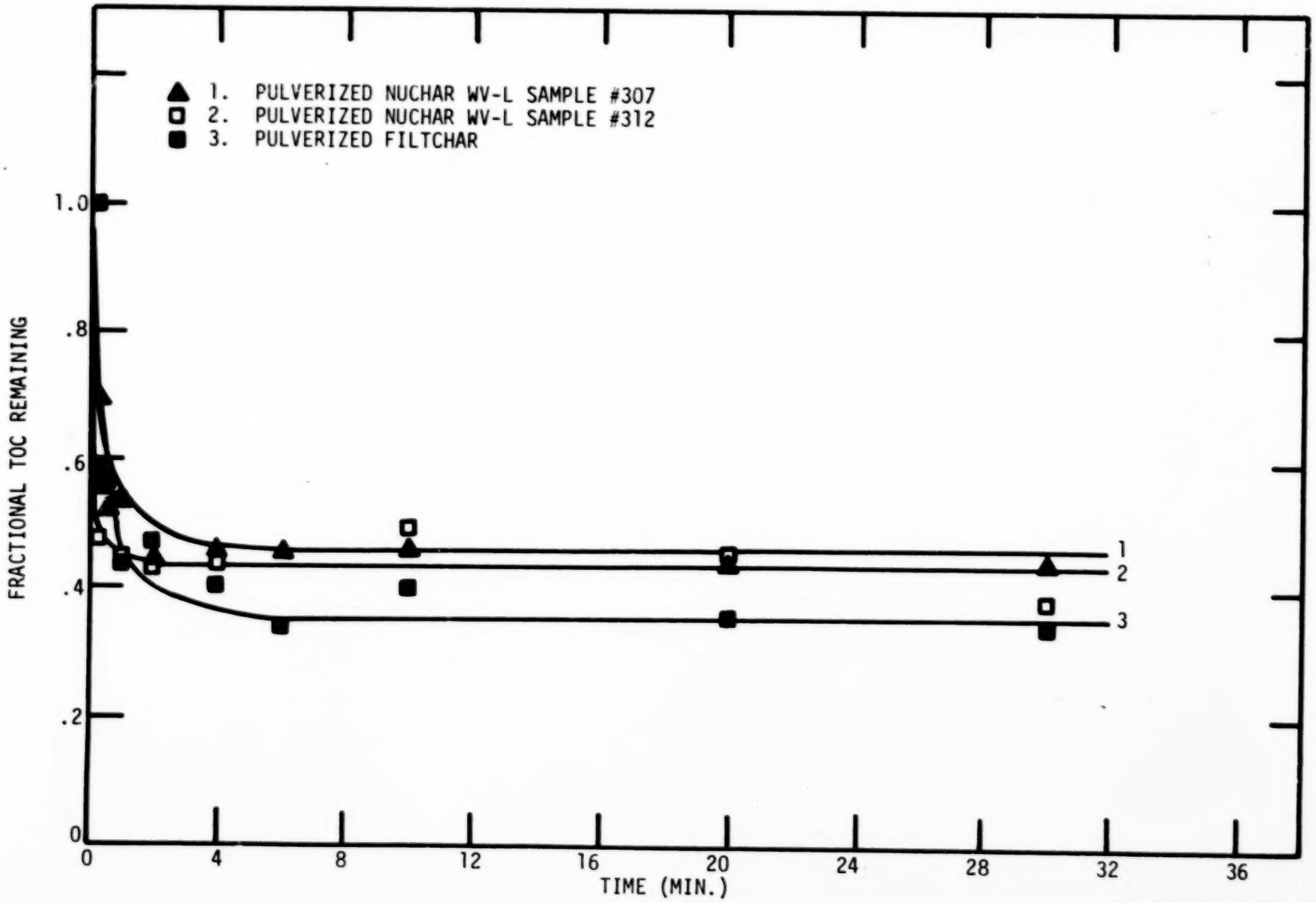

Figure 3. Rate of TOC adsorption
Roanoke, Virginia municipal secondary effluent

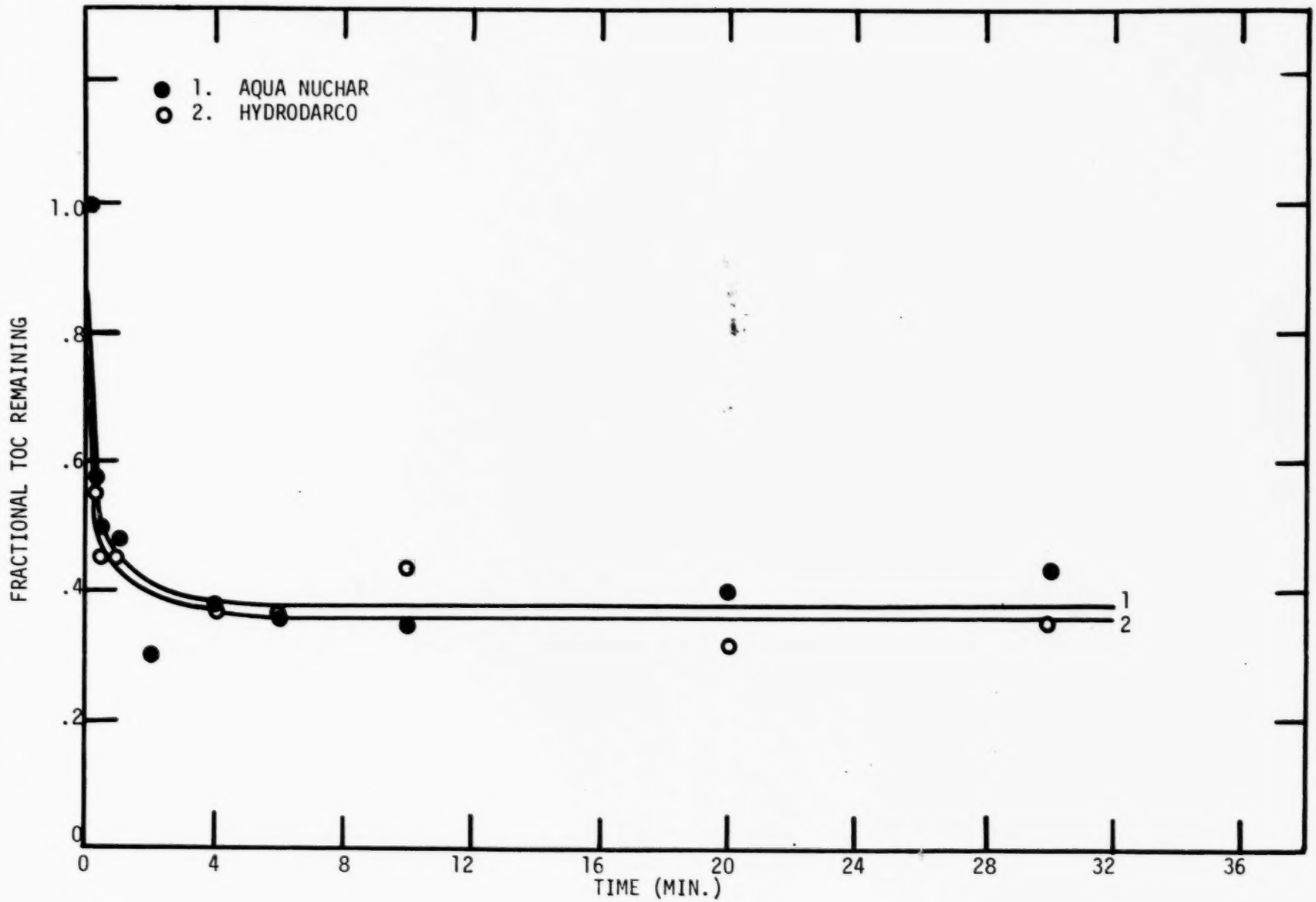

Figure 4. Rate of TOC adsorption
Roanoke, Virginia municipal secondary effluent

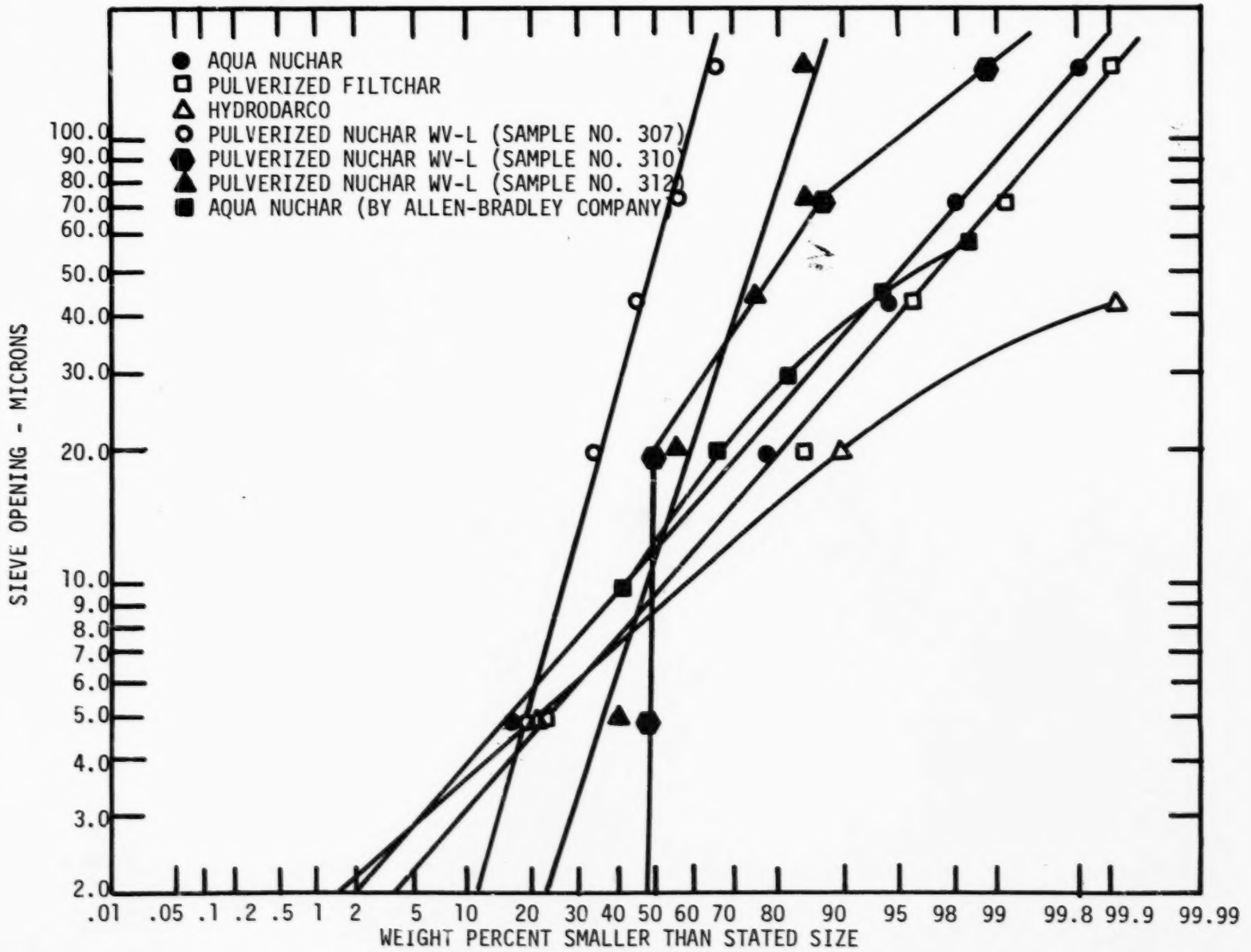

Figure 5. Particle size distributions of powdered carbons
February, 1968

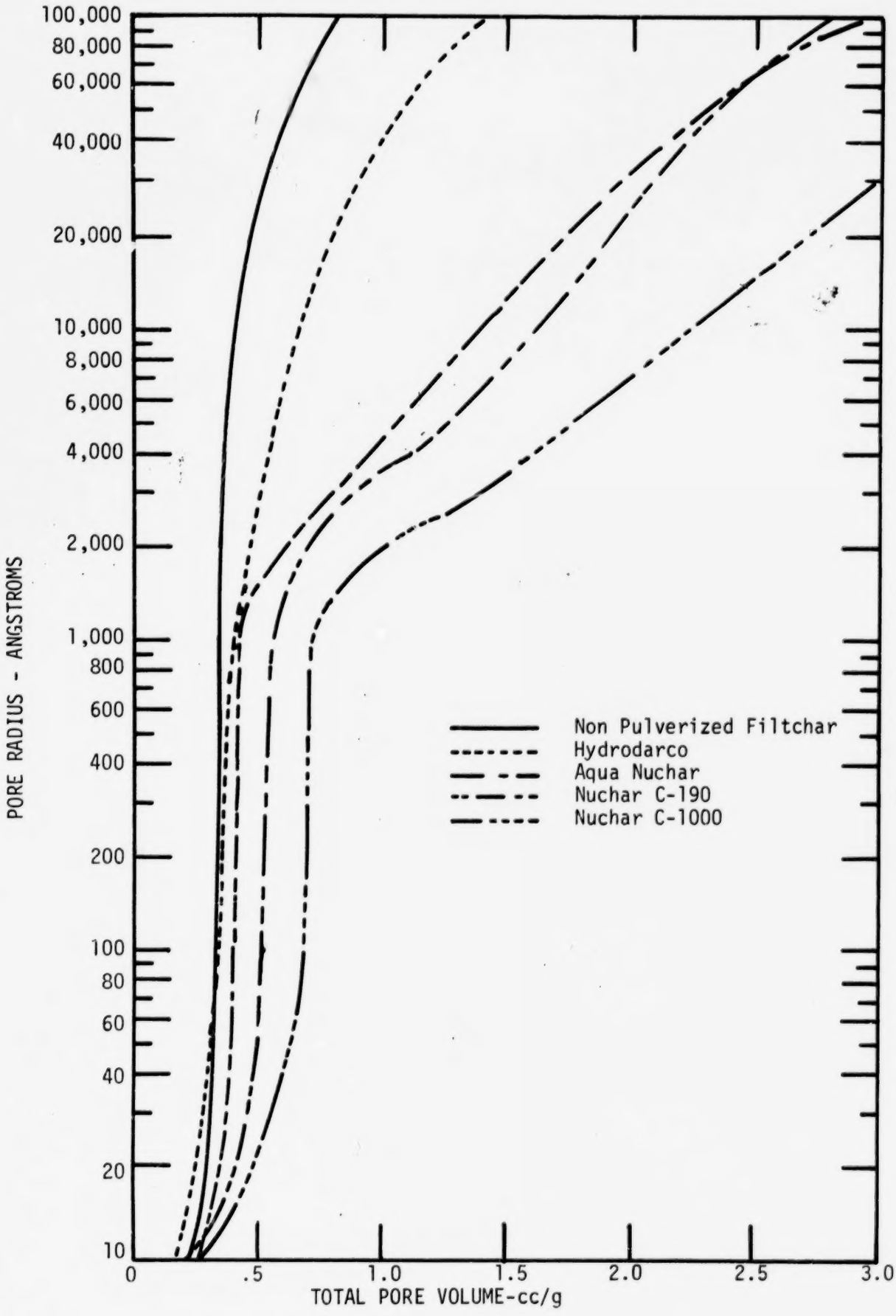

Figure 6. Pore volume distribution

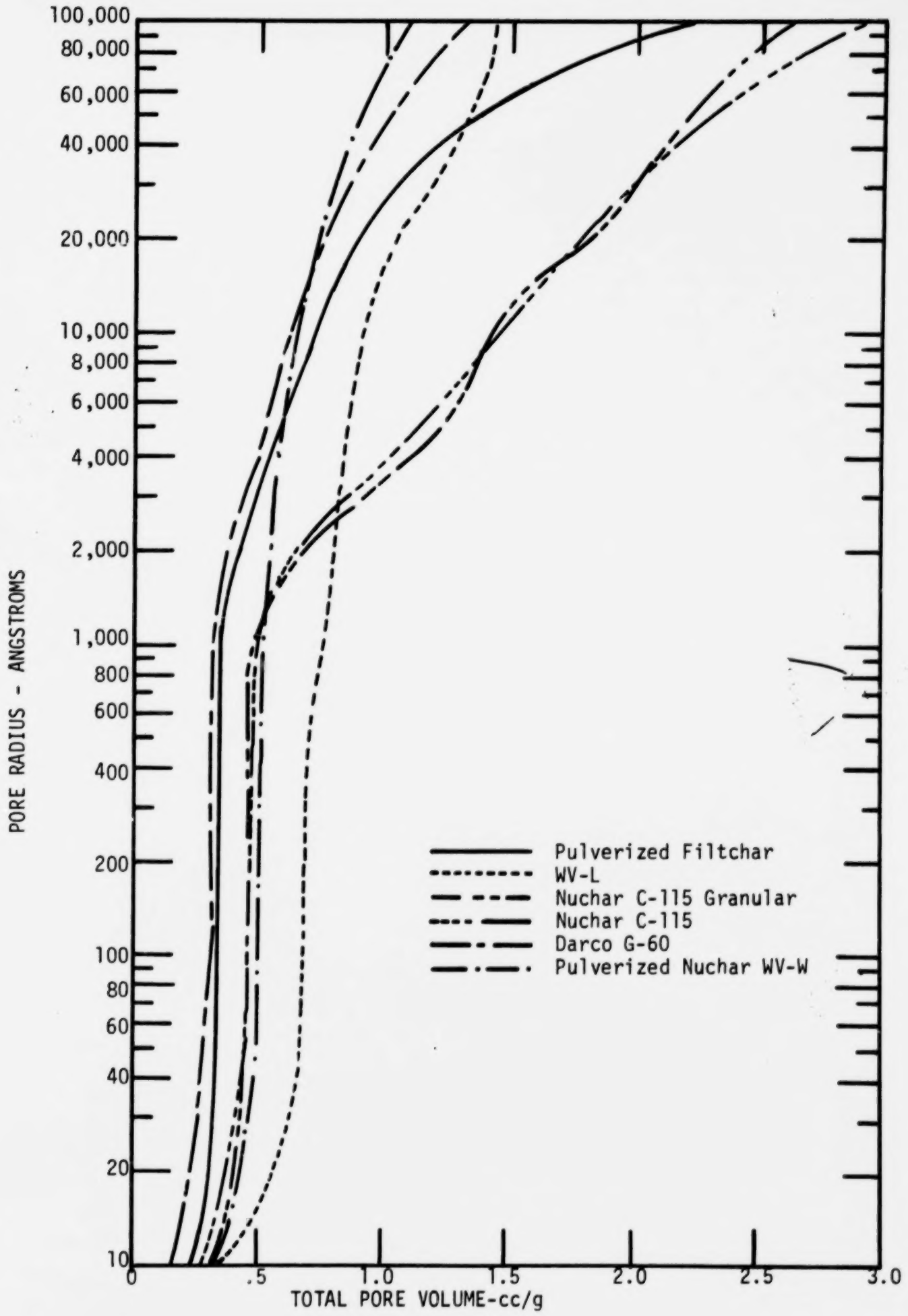

Figure 7. Pore volume distribution

CORRELATION OF CARBON PROPERTIES WITH TOC ADSORPTION CAPACITIES

One of the major aims of the present study has been to add to the understanding of the relationship between adsorptive capacities of powdered carbons for organic pollutants (TOC) and basic properties of the carbons. Since pore structure is known from previous studies to have a major influence on adsorptive properties, an extensive study in correlating TOC capacity and pore structure was undertaken. Correlations were made between both surface areas and pore volumes within various pore size ranges and TOC capacities. Also, correlations were made between Iodine Value and Decolorizing Index and TOC adsorption capacities.

As a measure of TOC capacity, TOC loadings at 25 and 75% of original filtered TOC concentrations were chosen for correlation. These loadings are obtained from Figures 1 and 2, which present TOC adsorption isotherms on municipal secondary effluent. Iodine Value and Decolorizing Index data are found in Table 1.

Pore volume and surface areas in various pore size ranges were obtained by the application of Roberts' method (8) to the nitrogen isotherms.

As a measure of the degree of correlation between the various parameters, the correlation coefficient was employed (9).

The formula for calculation of the correlation coefficient (r) is as follows:

$$r = \frac{N\Sigma XY - (\Sigma X)(\Sigma Y)}{\sqrt{[N\Sigma X^2 - (\Sigma X)^2][N\Sigma Y^2 - (\Sigma Y)^2]}}$$

where $\underline{X}$ and $\underline{Y}$ = parameters being correlated

$\underline{N}$ = number of observations (data points)

The larger the correlation coefficient, the greater the correlation between the parameters with a value of ±1.00 representing a perfect correlation.

The correlation coefficients between TOC adsorption capacity and surface areas and pore volumes within various pore size ranges are found in Tables 2 and 3.

Table 2

CORRELATION COEFFICIENTS BETWEEN TOC ADSORPTION CAPACITY AND SURFACE AREA IN PORES OF VARIOUS PORE RADIUS INTERVALS

Pore Radius Intervals - Angstroms	December Isotherms		January Isotherms	
	25% Initial TOC	75% Initial TOC	25% Initial TOC	75% Initial TOC
0-1000	0.73	0.75	0.43	0.33
10-1000	0.77	0.84	0.54	0.51
14-1000	0.91	0.79	0.63	0.71
16-1000	0.91	0.79	0.68	0.77
18-1000	0.89	0.79	0.70	0.79
20-1000	0.84	0.80	0.72	0.81
25-1000	0.80	0.69	0.58	0.76
30-1000	0.75	0.69	0.58	0.77
14-20	0.88	0.78	0.47	0.49
14-30	0.90	0.80	0.80	0.61
14-40	0.90	0.84	0.82	0.62
16-20	0.90	0.80	0.39	0.45
18-20	0.91	0.75	0.77	0.50
18-25	0.89	0.77	0.69	0.71
18-30	0.91	0.80	0.69	0.73
18-40	0.92	0.79	0.69	0.71

Table 3

CORRELATION COEFFICIENTS BETWEEN TOC ADSORPTION CAPACITY AND PORE VOLUME IN PORES OF VARIOUS PORE RADIUS INTERVALS

Pore Radius Intervals - Angstroms	December Isotherms		January Isotherms	
	25% Initial TOC	75% Initial TOC	25% Initial TOC	75% Initial TOC
0-10	0.39	0.53	0.09	0.10
0-30	0.72	0.78	0.45	0.40
0-100	0.80	0.83	0.53	0.52
0-1000	0.81	0.82	0.53	0.52
10-30	0.83	0.83	0.54	0.52
30-50	-0.24	-0.36	0.20	0.07
50-100	-0.48	-0.42	-0.12	0.04
100-1000	0.10	0.16	0.27	0.31
20-100	0.87	0.78	0.67	0.79
20-1000	0.82	0.70	0.64	0.75

Correlation coefficients between TOC adsorption capacity, and Iodine Values and Decolorizing Index values are found in Tables 4 and 5.

Table 4
CORRELATION COEFFICIENTS BETWEEN TOC ADSORPTION CAPACITY AND IODINE VALUE

% Equilibrium TOC	December Isotherms	January Isotherms
25	0.66	0.45
50	0.70	0.34
75	0.66	0.27
100	0.51	0.33

Table 5
CORRELATION COEFFICIENTS BETWEEN
TOC ADSORPTION CAPACITY AND MOLASSES DECOLORIZING INDEX

% Equilibrium TOC	December Isotherms	January Isotherms
25	0.87	0.62
50	0.83	0.79
75	0.78	0.80
100	0.72	0.80

The surface area data giving two of the higher correlation coefficients are presented in Figures 8 and 9. The data giving the best two correlation coefficients when considering pore volume in pores of various sizes are presented in Figures 10 and 11. Figures 12-15 present plots of Iodine Value and Decolorizing Index versus TOC adsorption capacities. These graphs also show the lines of regression.

The points in Figures 8-15 are labeled according to the carbons they represent. The numbers code for the carbons are:

1. Aqua Nuchar
2. Nuchar C-115
3. Nuchar C-115 Granular
4. Nuchar C-190
5. Nuchar C-1000
6. Pulverized Nuchar WV-W
7. Pulverized Nuchar WV-L
8. Pulverized Filtchar
9. Non-Pulverized Filtchar
10. Hydrodarco
11. Darco G-60

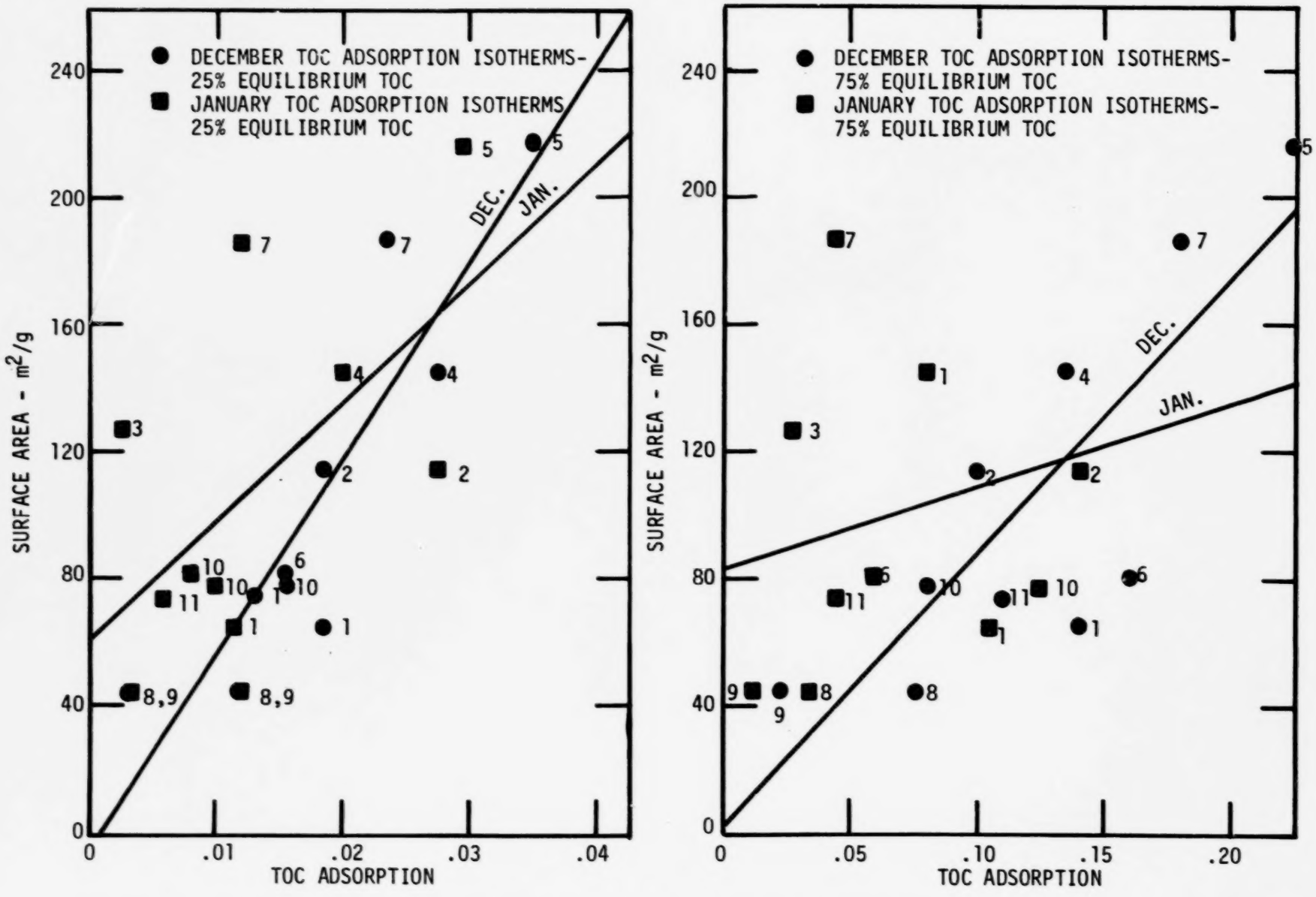

Figure 8. TOC adsorption versus surface area in pores of radii 14-40 angstroms

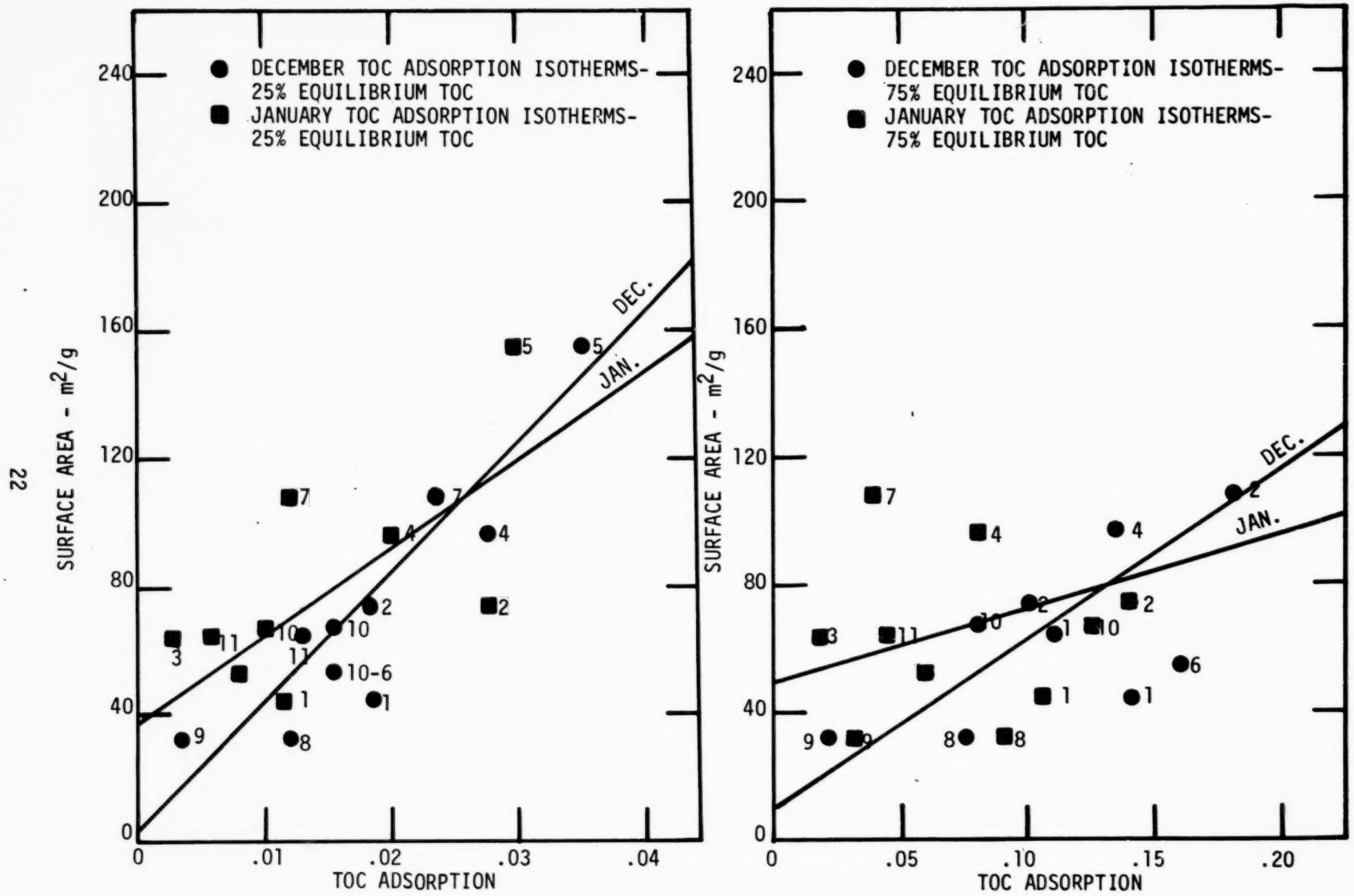

Figure 9. TOC adsorption versus surface area in pores greater than 16 angstroms in radius

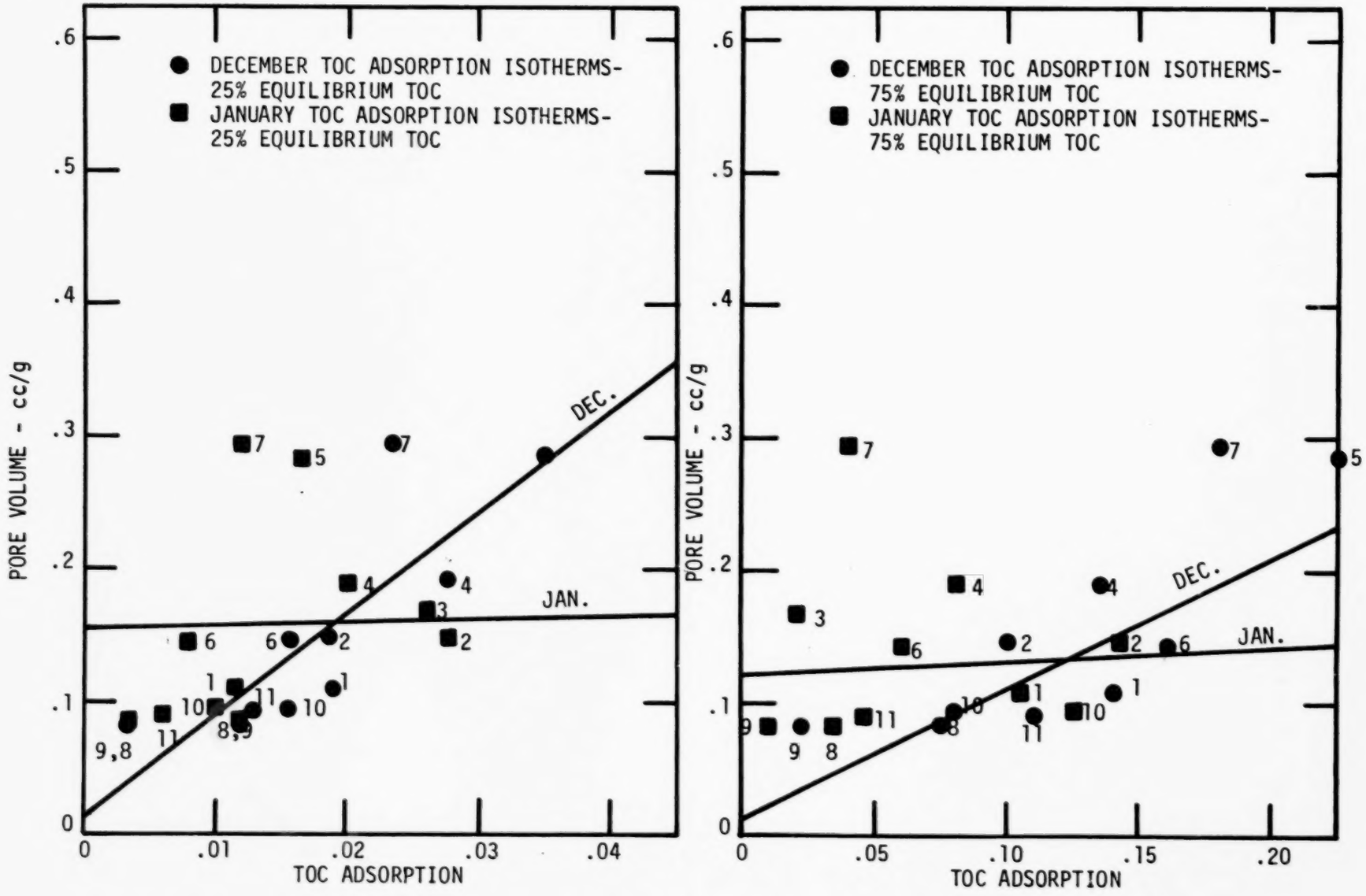

Figure 10. TOC adsorption versus pore volume in pores of radii 10-30 angstroms

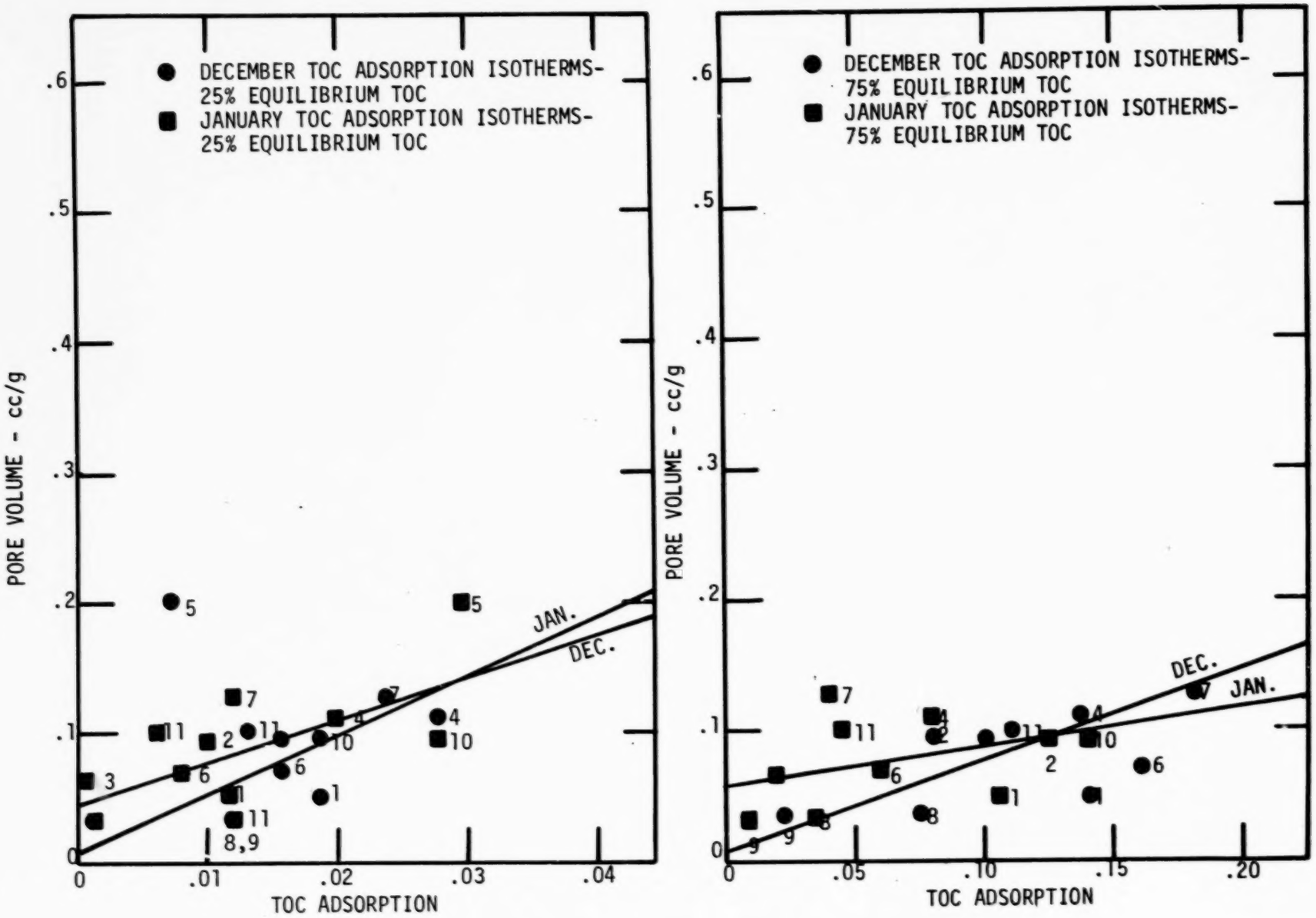

Figure 11. TOC adsorption versus pore volume in pores of radii 20-100 angstroms

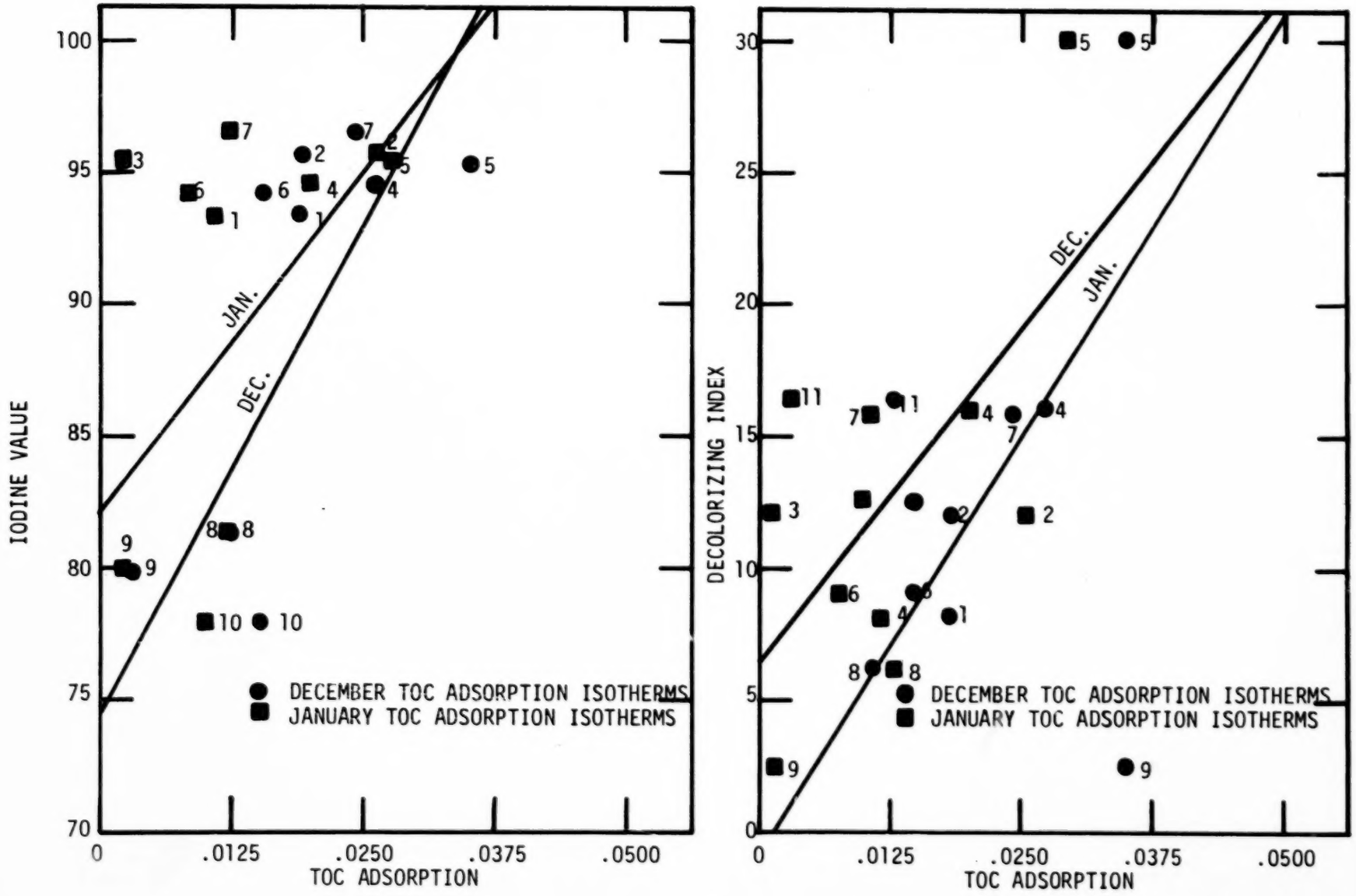

Figure 12. TOC adsorption versus IV and DI for 25% equilibrium TOC

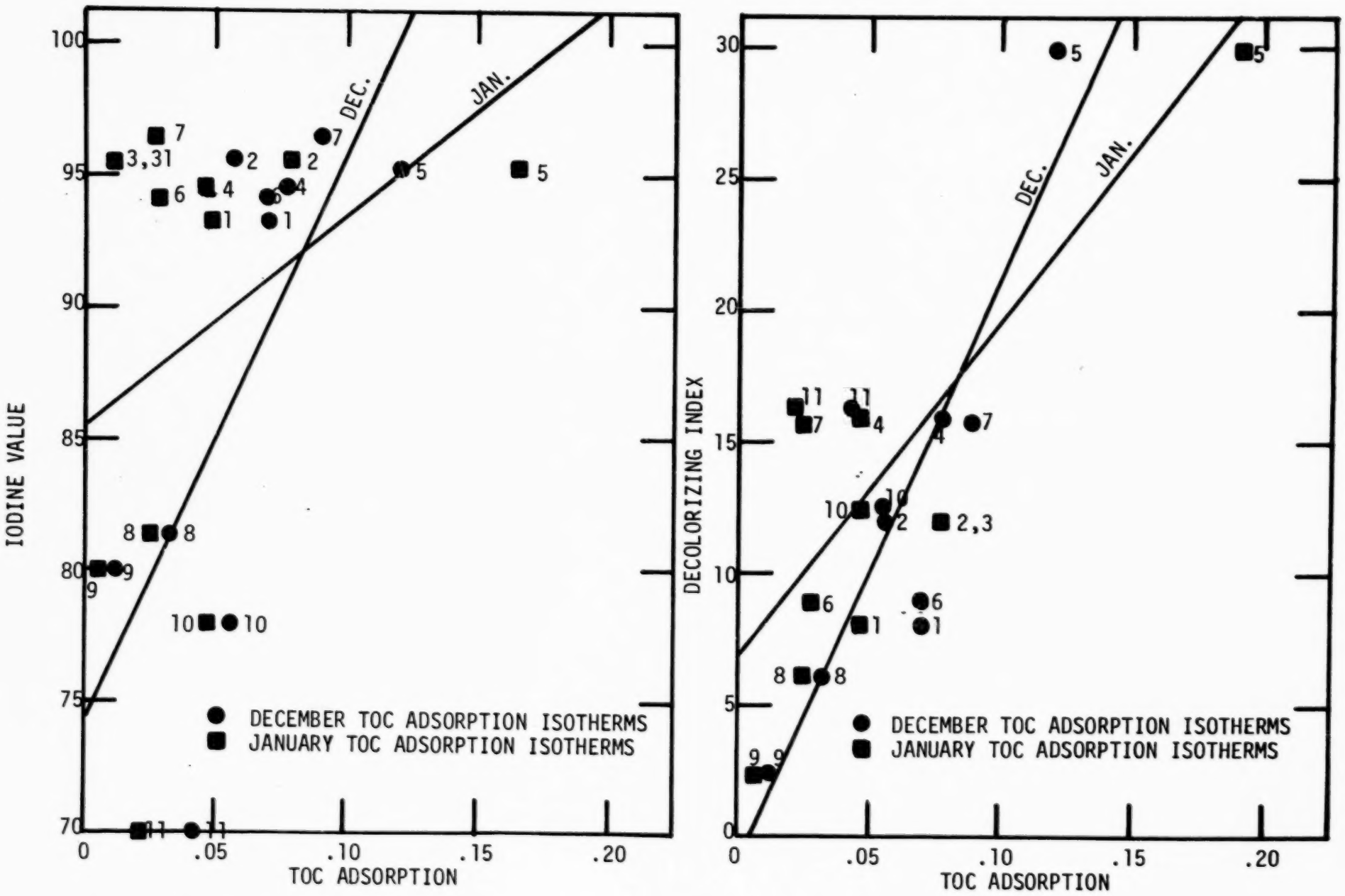

Figure 13. TOC adsorption versus IV and DI for 50% equilibrium TOC

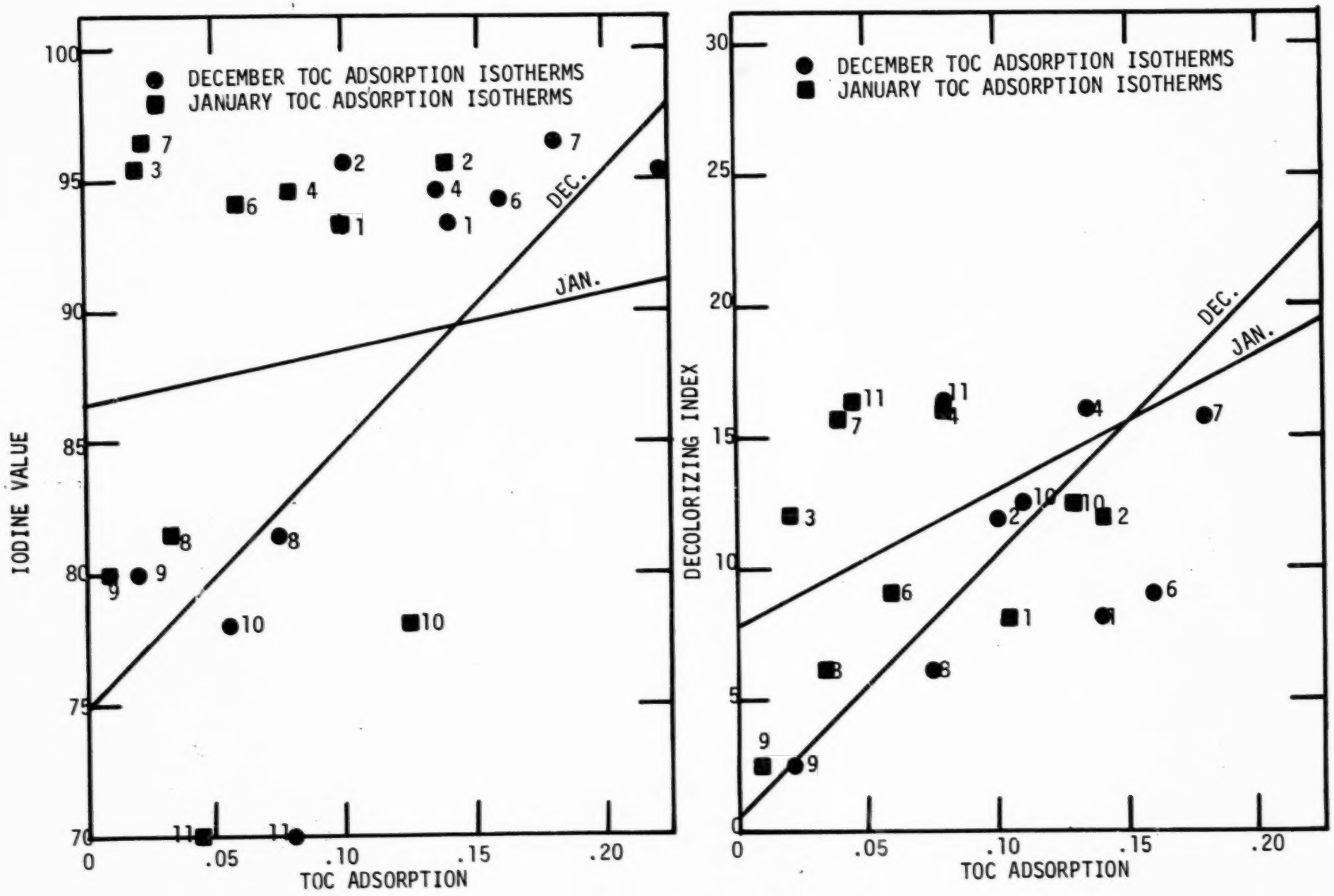

Figure 14. TOC adsorption versus IV and DI for 75% equilibrium TOC

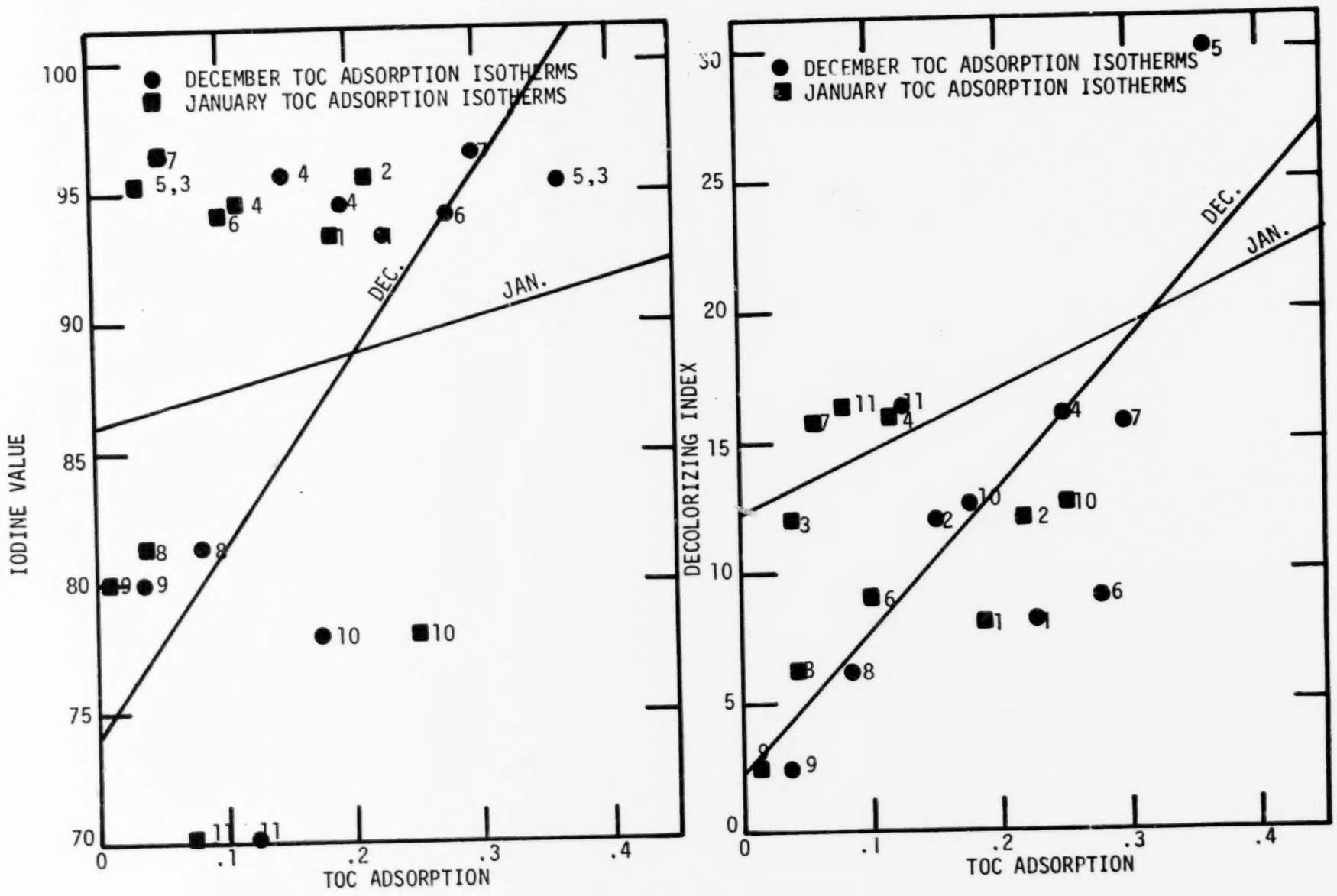

Figure 15. TOC adsorption versus IV and DI for 100% equilibrium TOC

DISCUSSION

It is seen from Figures 1 and 2 that many of the isotherms do not fit the Freundlich equation over the entire concentration range and, in fact, some become practically vertical. The Freundlich isotherm is described by the relation:

$$X/M = kC^{1/n}$$

where X/M is the adsorption capacity in terms, for example, of weight adsorbed per unit weight of carbon, C is the concentration of adsorbing substance at equilibrium (TOC in this case), and k and n are constants. If the Freundlich equation is obeyed, a log-log plot of X/M versus C produces a straight line. Adsorption of simple substances and simple mixtures onto activated carbon at low concentrations commonly follow the Freundlich isotherm.

One possible explanation for deviation from the Freundlich isotherm in this case is a positive constant error in the TOC analysis. This seems unlikely. Another, and more probable, explanation is that the waste water has some components which are much less strongly adsorbed than other components leading to quite different behavior at high and low carbon dosages. At high carbon dosages, necessary to produce equilibrium concentrations in the lower range, a residual TOC is left which is not removed by addition of further carbon. It is noticed that the tendency to leave a residual TOC not removed by further carbon is greatest for pulverized and granular Filtchar. This carbon, as indicated from its pore size distribution, has most of its pore volume in extremely small pores and thus apparently lacks large pores providing adsorptive capacity for higher molecular weight substances. One would expect the best carbon for treating municipal waste water to have a broad spectrum of pore sizes.

The pore size distributions in Figures 6 and 7 show some quite distinctive differences in pore structure between these powdered carbons. Pulverized Nuchar WV-L, Nuchar C-190, and Nuchar C-1000 are seen to have a quite broad distribution of pores in the size range responsible for adsorption equilibrium properties (these are micropore, roughly 0 to 100 Angstroms in radius). Filtchar has a very narrow distribution with most of its micropore volume in pores smaller than 10 Angstroms in radius. The other carbons have distributions of intermediate breadth.

It is interesting to note the characteristic extremely large volume possessed by the lignin based carbons, Aqua Nuchar, Nuchar C-115, Nuchar C-190, and Nuchar C-1000, in the pore size range 1,000 to 100,000 Angstroms in radius.

A comparison of the data in Tables 2 and 3 reveals that generally much higher correlation with TOC capacity is found for surface areas in various pore size intervals (Table 2) than for pore volumes in various intervals. Among the intervals tested, the highest correlation is seen with surface area in pores greater than about 14 Angstroms in radius and

with surface area in pores in the approximate range of 14-40 Angstroms. (Surface area in pores greater than 1,000 Angstroms is negligible.) It is not possible to tell which, if either, of these ranges is of primary importance. It may be, for example, that the 14-40 Angstrom range correlates well with TOC capacity only because there is a high correlation between surface area in the 14-40 Angstrom range and surface area in the 40-1,000 Angstrom range, or vice versa. In other words, they are not statistically independent. Even though the December isotherms almost always gave higher correlation coefficients than the January isotherms, the same trends are seen for both sets of data.

The high correlation of surface area in pores greater than a given size can be easily explained by a physical model which visualizes only the surface area in pores larger than the adsorbing materials being accessible for adsorption. Surface area in pores smaller than the adsorbing molecules contribute nothing to the adsorptive capacity, since the molecules cannot enter these pores.

In correlations of pore structure with TOC capacity (Figures 8 through 11), it is seen that Aqua Nuchar gives consistently higher TOC capacities than expected from the line of regression, while C-1000 gives a lower than expected capacity. From the pore size distributions, Aqua Nuchar is known to have a small average pore size while Nuchar C-1000 has a large average pore size. The same trend is seen in other carbons, those with small average pore size giving higher than expected capacity. This is perhaps not too surprising since it is known that the tenacity of adsorption is greater in small pores than in larger ones, thus for equal available surface area the smaller pored carbons might be expected to have a higher capacity.

Correlations of TOC adsorption capacity and Iodine Value and Decolorizing Index are found in Tables 4 and 5, respectively. The Iodine Value and Decolorizing Index tests were chosen for correlation studies since both are common standard carbon tests and are relatively simple to perform. A high correlation was found to exist for the Decolorizing Index test and a low correlation for the Iodine Value test, as is apparent from these data. In view of the pore structure results, the Decolorizing Index test would, in fact, be expected to show a high degree of correlation with TOC, since this test is known from previous work to indicate surface area in pores greater than approximately 14 Angstroms in radius. These are, of course, essentially the same pores which gave the highest correlations with TOC capacity.

It is not clear whether the imperfect correlation of TOC capacity with pore structure is due to errors in measurement of TOC capacity, pore structure parameters, or a discrepancy in the model. Certainly there is a wide variety of compounds contributing to TOC in municipal effluent.

It is interesting to note that a better correlation can be obtained between Decolorizing Index and pore structure than between TOC capacity and pore structure. A correlation coefficient of 0.97 was obtained for the correlation with pore volume in pores between 20 and 100 Angstroms radius.

The suspendability was selected as an indication of carbon settling characteristics and was performed on all carbons. The results are shown in Table 1. Increased speed of settling could influence strongly the size of clarifiers and need for flocculating aids. It was encouraging to note that pulverized Nuchar WV-W, pulverized Nuchar WV-L and non-pulverized Filtchar gave much lower suspendability results than the other carbons. These carbons should be tested in a continuous adsorption system.

The rate of adsorption curves for Aqua Nuchar, Hydrodarco, pulverized Nuchar WV-L and pulverized Filtchar, Figures 3 and 4, shows that at least 95% of the TOC ultimately removed was adsorbed within four minutes.

The particle size distributions for Aqua Nuchar, Hydrodarco and pulverized Filtchar, Figure 5, show these carbons to have medium particle sizes of about 10 microns. The pulverized Nuchar WV-L samples were found to be somewhat coarser with median particle sizes of 55, 19 and 13 microns for samples numbered 307, 310 and 312, respectively. The difference in particle size of the pulverized Nuchar WV-L, numbers 307 and 312, is reflected in the rate of adsorption studies. The coarser WV-L, sample number 307, was considerably slower than WV-L, sample number 312. The observation of slower rate of adsorption for large particle size is in agreement with the observation of many previous workers in granular carbons. It is not surprising that the same should be seen in the powdered carbons.

Figure 5 shows that the particle size distribution of Aqua Nuchar is in agreement with distributions of this material by several other methods. The median particle size for Aqua sample was 12 microns and is in close agreement with the medium particle size of 11 microns found by other methods (3).

Other things equal, the carbon requiring the least expenditure to treat municipal waste water would be the one which has the highest TOC adsorptive capacity/cost ratio. The capacity should be measured at the TOC of the water passing from the first to the second stage, in a two-stage countercurrent system, since this will be the loading on the spent carbon removed for disposal or regeneration.

An average TOC adsorptive capacity was determined from the December and January adsorption isotherms at a TOC concentration of 15 mg/l. As mentioned above, loading at the intermediate concentration is the critical loading to use in a two-stage countercurrent process, since this will give an indication of carbon usage or rate of exhaustion.

Table 6 shows this ratio calculated from the present data.

Table 6
TOC ADSORPTIVE CAPACITY/COST RATIO

Carbon	TOC Adsorptive Capacity/Cost (g TOC Adsorbed/¢)
Hydrodarco	5.42
Aqua Nuchar	5.00
Nuchar C-115	3.59
Nuchar C-190	2.48
Nuchar C-1000	1.71
Darco G-60	0.48
Pulverized Nuchar WV-W	-
Pulverized Nuchar WV-L	-
Pulverized Filtchar	-
Non-Pulverized Filtchar	-

In terms of adsorptive capacity per unit cost, it is seen that Aqua Nuchar and Hydrodarco are by far the superior carbons with ratios of 5.00 and 5.42, respectively. These two carbons are followed in effectiveness by Nuchar C-115 and Nuchar C-190. Costs were not calculated for pulverized Nuchar WV-L, Nuchar WV-W, and pulverized and non-pulverized Filtchar, since these are non-commercial carbons.

CONCLUSIONS

In terms of TOC adsorptive capacity per unit cost for a two-stage countercurrent adsorption system to treat municipal waste water, Aqua Nuchar and Hydrodarco, of the commercial powdered carbons evaluated, are by far the superior carbons.

The experimental coal-based carbons, pulverized Nuchar WV-L and Nuchar WV-W, showed clear superiority in settling characteristics, as measured by the Suspendability Test. This is probably due to the much higher density and somewhat greater particle sizes of the coal-based carbons.

Pulverized Nuchar WV-L and Nuchar C-1000 were seen to have quite broad pore size distributions in the micropore range, 0-1000 Angstrom radius. Filtchar A had a very narrow distribution. The other carbons had intermediate distributions.

A fairly good correlation was found between TOC adsorptive capacity and pore structure. The pore structure parameter giving the best correlation was surface area in pores greater than about 14 Angstroms in radius. Surface area in pores 14-40 Angstroms in radius gave a good correlation as well. It was seen that carbons with small average pore sizes gave better than expected TOC capacities while carbons with large average pore sizes gave poorer than expected capacities. This may be explained by the greater tenacity of adsorption known to exist in smaller pores.

The ideal carbon should have a broad spectrum of pore sizes so as to accommodate the wide variety of molecules present in waste waters. Perhaps mixtures of carbons of different pore structure characteristics would be most efficient.

Decolorizing Index gave practically as good correlation with TOC adsorptive capacity as pore structure.

In batch rate of adsorption experiments, Aqua Nuchar, Hydrodarco, pulverized Nuchar WV-L and pulverized Filtchar were seen to adsorb 95% of the TOC ultimately removed within 4 minutes. As expected from previous studies on granular carbons, rate of adsorption of a powdered carbon was seen to be strongly influenced by its particle size.

The lignin-based carbons were seen to have unusually large volumes in pores in the 1,000 to 100,000 Angstrom radius range.

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27 Abstract:

Eleven commercial and experimental powdered activated carbons were subjected to an intensive laboratory evaluation of their physical and adsorptive properties to select those best suited to treating municipal waste water and to gain insight into properties important for this application. Measurements were made of TOC (Total Organic Carbon) adsorption isotherms from Roanoke, Virginia municipal secondary effluent, pore structure, BET surface area, molasses value, decolorizing index, iodine value, real density, suspendability, and apparent density. Correlations were made between capacities for adsorbing organic impurities from municipal secondary effluent, as measured by TOC adsorptive capacities, and carbon properties such as iodine value, molasses decolorizing index and pore structure.

Aqua Nuchar and Hydrodarco were clearly superior to other commercial grades tested in TOC adsorptive capacity per unit cost. The coal-base experimental carbons, pulverized Nuchar WV-L and Nuchar WV-W, were indicated by the suspendability test to be more easily removed than other carbons.

Abstractor

WR:102 (REV WRSIC)

Among many pore structure parameters compared, surface area in pores greater than approximately 14 Angstroms in radius was found to give the best correlation with TOC capacity. However, the correlation was not perfect, the correlation coefficient being 0.91. TOC adsorptive capacity was indicated reasonably well by the decolorizing index test. Here, correlation coefficients in the 0.80's were obtained. It is suggested that the best carbon for adsorbing organics from municipal wastes have a broad spectrum of pore sizes. Particle size of the powdered carbons was found to strongly affect the rate of adsorption.

Aqua Nuchar, Hydrodarco, and pulverized Nuchar WV-L are recommended for further study.

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